

A mixed iron(III)/lithium alkoxide

Helen R. L. Barley, Alan R. Kennedy* and Robert E. Mulvey

WestCHEM, Department of Pure and Applied Chemistry, University of Strathclyde, 295 Cathedral Street, Glasgow G1 1XL, Scotland
Correspondence e-mail: a.r.kennedy@strath.ac.uk

Received 5 May 2005

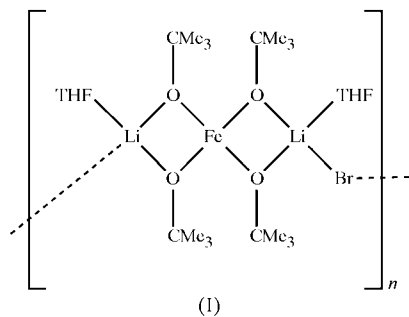
Accepted 3 June 2005

Online 22 June 2005

The heterometallic alkoxide *catena*-poly[[tetra- μ_2 -*tert*-butoxo-1:2 κ^4 O:O;1:3 κ^4 O:O-bis(tetrahydrofuran)-2 κ O,3 κ O-iron(III)-dilithium(I)]- μ -bromo], $[\text{FeLi}_2\text{Br}(\text{C}_4\text{H}_9\text{O})_4(\text{C}_4\text{H}_8\text{O})_2]_n$, forms a one-dimensional chain through an *a*-glide. This conformation is achieved through the formation of $\text{Fe}^{\text{III}}/\text{O}/\text{Li}/\text{O}$ rings and $\text{Li}-\text{Br}-\text{Li}$ bridges.

Comment

Currently, our group is investigating the synthetic and structural synergic effects that can be harnessed by mixing an alkali metal and magnesium in the same molecular amide environment [for pertinent recent examples, see Hevia *et al.* (2005) and Andrikopoulos *et al.* (2004)]. One possible outcome of this mixed-metal-induced synergy is to generate 'inverse crown' ring systems in which Lewis acidic polymetallic cationic host rings surround Lewis basic anionic cores, as recently described for the oxo-centred 2,2,6,6-tetramethylpiperidinide (TMP) inverse crown 'ether' $[\text{Na}_2\text{Mg}_2\text{O}(\text{TMP})_4]$ (Kennedy *et al.*, 2003). Germane to the work reported here, another type of inverse crown motif involves a chair-shaped octagonal ring that is face-capped on opposite sides of the chair by, for example, alkoxide ligands, as demonstrated by the mixed lithium–magnesium diisopropylamideoctoxide $[\{\text{LiMg}[\text{N}(\text{Pr})_2]_2^{\text{n}}\text{OctO}\}_2]$ (Drewette *et al.*, 2002). This motif bears a



close similarity to that of the mixed sodium–iron(II) butoxide $[\{(\text{THF})\text{NaFe}(\text{BuO})_3\}_2]$ (THF is tetrahydrofuran) reported by Gun'ko *et al.* (2002), which, in our terminology, could be regarded as an all-alkoxide inverse crown. Wishing to pursue

this structural analogy further, we attempted to prepare the lithium congener $[\{(\text{THF})_x\text{LiFe}(\text{BuO})_3\}_2]$ by carrying out a metathetical reaction between FeBr_2 and three molar equivalents of BuOLi in THF solution. This attempt failed as the metathesis did not go to completion and the iron in the product oxidized to Fe^{III} , presumably as a result of the strong oxidizing nature of alkoxide ligands. The product obtained was the bromide-containing compound $[\{(\text{THF})_2\text{Li}_2\text{Fe}(\text{BuO})_4\text{Br}\}_\infty]$, (I). Such heterometallic alkoxide compounds are of interest as precursors to oxide-based materials (Bradley, 1989; Bradley *et al.*, 2001).

The asymmetric unit of (I) (Fig. 1) consists of a central Fe^{III} atom bonded to four BuO ligands that bridge two Li atoms. The coordination about atom Fe1 is considerably distorted from tetrahedral geometry [$\text{O}-\text{Fe1}-\text{O} = 89.60(5)-121.60(5)^\circ$; Table 1], the narrowest angles, as expected, being those internal to the $\text{Fe}/\text{O}/\text{Li}/\text{O}$ rings. The $\text{Fe}-\text{O}$ bond lengths span a tight range [$1.8616(11)-1.8687(11) \text{ \AA}$], and are significantly shorter than those that bridge Fe atoms in $[(\text{BuO})_2\text{Fe}(\mu\text{-BuO})_2\text{Fe}(\text{BuO})_2]$ ($1.958-1.961 \text{ \AA}$; Spandl *et al.*, 2003). This difference presumably reflects greater competition for the O-atom electron density between two Fe atoms as opposed to between an Fe and an Li atom. In (I), the $\text{Li}-\text{OBU}$ distances [$1.958(3)-1.991(3) \text{ \AA}$] are greater than the $\text{Fe}-\text{OBU}$ distances. This configuration contrasts with that of one of the few known structures featuring alkoxides bridging between Fe^{III} and Li atoms. In $[(\text{Bu}_2\text{CHO})_2\text{Fe}(\mu\text{-Bu}_2\text{CHO})_2]$

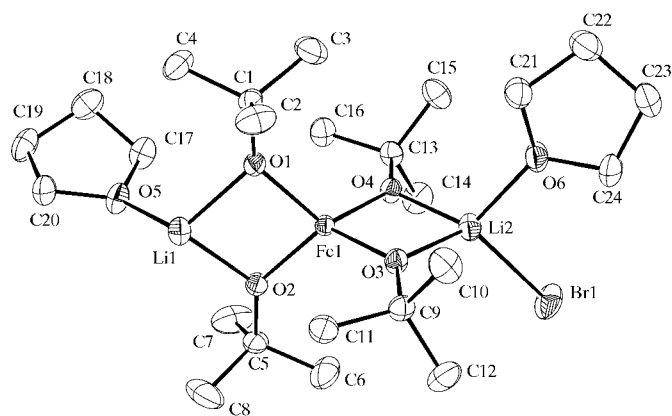


Figure 1

The asymmetric unit of (I), with 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

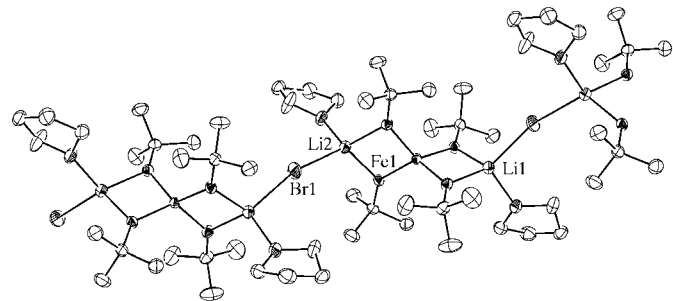


Figure 2

An illustration of the propagation of (I) in the *a* direction to form a polymeric chain.

Li(Bu₂CHOH)] (Bochmann *et al.*, 1980), the situation is reversed, with Fe—O bridges of 1.908 and 1.934 Å, and Li—O distances of 1.870 and 1.874 Å; the difference appears to be that lithium is three-coordinate in this complex and four-coordinate in (I). In (I), the bonding at each Li atom is completed by complexation of a THF molecule and of a Br atom, thus forming an Li—Br—Li bridge that extends (I) into a one-dimensional polymer, propagating through an *a*-glide (Fig. 2).

Experimental

FeBr₂ (1.078 g, 5 mmol) and Li(^tBuO) (1.20 g, 15 mmol) were weighed out in a glove-box and transferred to a Schlenk tube filled with dry argon. The tube was placed on a vacuum line and cooled to 273 K in an ice bath. THF (20 ml) was added *via* syringe and the brown mixture was stirred at room temperature overnight. The next day, the mixture was filtered through Celite to remove LiBr and washed with THF (10 ml). The solution was reduced in volume under vacuum and left to stand overnight. A large crop of crystals formed in the dark-brown solution. The crystals were not single, and so were redissolved by gentle heating and placed in a water bath to cool slowly. Overnight, suitable higher-quality crystals of (I) formed (yield 18.15%). Microanalysis expected: C 49.17, H 8.94%; found: C 48.36, H 8.60%.

Crystal data

[FeLi ₂ Br(C ₄ H ₉ O) ₄ (C ₄ H ₈ O) ₂]	$D_x = 1.243 \text{ Mg m}^{-3}$
$M_r = 586.30$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/a$	Cell parameters from 34588 reflections
$a = 18.4449$ (5) Å	$\theta = 1.0\text{--}27.5^\circ$
$b = 9.0987$ (3) Å	$\mu = 1.79 \text{ mm}^{-1}$
$c = 18.6750$ (5) Å	$T = 123$ (2) K
$\beta = 90.535$ (2)°	Prism, pale yellow
$V = 3133.99$ (16) Å ³	$0.50 \times 0.45 \times 0.40 \text{ mm}$
$Z = 4$	

Table 1

Selected geometric parameters (Å, °).

Fe1—O4	1.8616 (11)	O2—Li1	1.973 (3)
Fe1—O1	1.8653 (11)	O1—Li1	1.970 (3)
Fe1—O3	1.8680 (11)	O4—Li2	1.958 (3)
Fe1—O2	1.8687 (11)	O3—Li2	1.991 (3)
Br1—Li2	2.471 (3)	O5—Li1	1.963 (3)
Br1—Li1 ⁱ	2.472 (3)	O6—Li2	1.979 (3)
O4—Fe1—O1	118.19 (5)	O4—Li2—O3	83.60 (11)
O4—Fe1—O3	89.80 (5)	O6—Li2—O3	113.49 (15)
O1—Fe1—O3	121.60 (5)	O4—Li2—Br1	118.39 (13)
O4—Fe1—O2	120.97 (5)	O6—Li2—Br1	101.04 (11)
O1—Fe1—O2	89.60 (5)	O3—Li2—Br1	124.83 (14)
O3—Fe1—O2	119.94 (5)	O5—Li1—O1	115.21 (15)
Li2—Br1—Li1 ⁱ	161.93 (10)	O5—Li1—O2	111.73 (15)
Fe1—O2—Li1	92.77 (10)	O1—Li1—O2	83.71 (11)
Fe1—O1—Li1	92.96 (10)	O5—Li1—Br1 ⁱⁱ	104.79 (12)
Fe1—O4—Li2	93.87 (10)	O1—Li1—Br1 ⁱⁱ	112.23 (13)
Fe1—O3—Li2	92.61 (9)	O2—Li1—Br1 ⁱⁱ	128.44 (14)
O4—Li2—O6	116.21 (16)		

Symmetry codes: (i) $x - \frac{1}{2}, -y + \frac{3}{2}, z$; (ii) $x + \frac{1}{2}, -y + \frac{3}{2}, z$.

Data collection

Nonius KappaCCD diffractometer	5934 reflections with $I > 2\sigma(I)$
ω and φ scans	$R_{\text{int}} = 0.039$
Absorption correction: multi-scan (SORTAV; Blessing, 1997)	$\theta_{\text{max}} = 27.5^\circ$
$T_{\text{min}} = 0.460, T_{\text{max}} = 0.497$	$h = -23 \rightarrow 23$
35132 measured reflections	$k = -11 \rightarrow 11$
7143 independent reflections	$l = -24 \rightarrow 24$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0243P)^2 + 1.8098P]$
$R[F^2 > 2\sigma(F^2)] = 0.029$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.070$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.03$	$\Delta\rho_{\text{max}} = 0.50 \text{ e \AA}^{-3}$
7143 reflections	$\Delta\rho_{\text{min}} = -0.59 \text{ e \AA}^{-3}$
319 parameters	
H-atom parameters constrained	

All H atoms were constrained to an idealized geometry using a riding model [for CH₃, $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ and C—H = 0.98 Å; for CH₂, $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ and C—H = 0.99 Å].

Data collection: DENZO (Hooft, 1988) and COLLECT (Otwinowski & Minor, 1997); cell refinement: DENZO and COLLECT; data reduction: DENZO; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEPII (Johnson, 1976); software used to prepare material for publication: SHELXL97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SF1003). Services for accessing these data are described at the back of the journal.

References

- Andrikopoulos, P. C., Armstrong, D. R., Clegg, W., Gilfillan, C. J., Hevia, E., Kennedy, A. R., Mulvey, R. E., O'Hara, C. T., Parkinson, J. A. & Tooke, D. M. (2004). *J. Am. Chem. Soc.* **126**, 11612–11620.
- Blessing, R. H. (1997). *J. Appl. Cryst.* **30**, 421–426.
- Bochmann, M., Wilkinson, G., Young, G. B., Hursthouse, M. B. & Malik, K. M. A. (1980). *J. Chem. Soc. Dalton Trans.* pp. 1863–1871.
- Bradley, D. C. (1989). *Chem. Rev.* **89**, 1317–1322.
- Bradley, D. C., Mehrotra, R. C., Rothwell, I. P. & Singh, A. (2001). In *Alkoxo and Aryloxo Derivatives of Metals*. London: Academic Press.
- Drewette, K. J., Henderson, K. W., Kennedy, A. R., Mulvey, R. E., O'Hara, C. T. & Rowlings, R. B. (2002). *Chem. Commun.* pp. 1176–1177.
- Gun'ko, Y. K., Cristmann, U. & Kessler, V. G. (2002). *Inorg. Chem.* pp. 1029–1031.
- Hevia, E., Honeyman, G. W., Kennedy, A. R., Mulvey, R. E. & Sherrington, D. C. (2005). *Angew. Chem. Int. Ed.* **44**, 68–72.
- Hooft, R. (1988). COLLECT. Nonius BV, Delft, The Netherlands.
- Johnson, C. K. (1976). ORTEPII. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Kennedy, A. R., MacLellan, J. G. & Mulvey, R. E. (2003). *Acta Cryst.* **C59**, m302–m303.
- Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
- Sheldrick, G. M. (1997). SHELXS97 and SHELXL97. University of Göttingen, Germany.
- Spandl, J., Kusserow, M. & Bradgam, I. (2003). *Z. Anorg. Allg. Chem.* **629**, 968–974.